

**IN THE UNITED STATES DISTRICT COURT
FOR THE NORTHERN DISTRICT OF ILLINOIS**

**IDEX CORP., EASTERN PLASTICS, INC.,
PULSAFEEDER, INC., AND
FELICE DIMASCIO,**

Plaintiffs,

vs.

**DRIPPING WET WATER, INC.,
ALLISON H. SAMPSON, and
RICHARD L. SAMPSON,**

Defendants.

**DRIPPING WET WATER, INC.,
ALLISON H. SAMPSON, and
RICHARD L. SAMPSON,**

Counterclaimants,

Vs.

**IDEX CORP., EASTERN PLASTICS, INC.,
PULSAFEEDER, INC., and
FELICE DIMASCIO,**

Counterdefendants.

Case No.: 08 C 1114

**Hon. Milton I. Shadur
Senior U.S. District Judge**

JURY TRIAL DEMANDED

**THE DWW PARTIES' ANSWER, AFFIRMATIVE DEFENSES,
AND COUNTERCLAIM**

Defendants and Counterclaimants Dripping Wet Water, Inc., Allison H. Sampson and Richard L. Sampson (hereinafter collectively “the DWW Parties” or “Counterclaimants”), file this Answer, Affirmative Defenses and Counterclaim to the First Amended Complaint for Declaratory Judgment (“the Complaint”) served by IDEX Corporation, Eastern Plastics, Inc. Pulsafeeder, Inc. and Felice DiMascio (hereinafter collectively “the IDEX Parties” or “Counterdefendants”).

NATURE OF THIS ACTION

1. The DWW Parties admit that the IDEX Parties allege a cause of action under the Declaratory Judgment Act 28 USC Sections 2201 and 2202 and deny the remaining allegations as set forth in Paragraph 1 of the First Amended Complaint.

2. The DWW Parties deny the allegations of Paragraph 2 of the First Amended Complaint

JURISDICTION AND VENUE

3. The DWW Parties admit the allegations of Paragraph 3 of the First Amended Complaint.

4. The DWW Parties admit the allegations of Paragraph 4 of the First Amended Complaint.

THE PARTIES

5. The DWW Parties admit that IDEX is a Delaware corporation with its principal place of business located in Northbrook, Illinois. The DWW Parties lack sufficient information to form a belief as to the truth or falsity of the remaining allegations set forth

in Paragraph 5 of the First Amended Complaint, and therefore denies them.

6. The DWW Parties admit that Eastern Plastics is a Connecticut corporation with its principal place of business located at 110 Balcyon Drive, Bristol, Connecticut. The DWW Parties lack sufficient information to form a belief as to the truth or falsity of the remaining allegations set forth in Paragraph 6 of the First Amended Complaint, and therefore denies them.

7. The DWW Parties admit that Pulsafeeder is a Delaware corporation with its principal place of business located in New York and Florida. The DWW Parties lack sufficient information to form a belief as to the truth or falsity of the remaining allegations set forth in Paragraph 7 of the First Amended Complaint, and therefore denies them.

8. The DWW Parties admit that Felice DiMascio is a citizen and resident of Connecticut. The DWW Parties lack sufficient information to form a belief as to the truth or falsity of the remaining allegations set forth in Paragraph 8 of the First Amended Complaint, and therefore denies them.

9. The DWW Parties admit the allegations of Paragraph 9 of the First Amended Complaint.

10. The DWW Parties admit the allegations of Paragraph 10 of the First Amended Complaint.

BACKGROUND

11. The DWW Parties admit that chlorine oxide (ClO_2) is a highly effective, environmentally-friendly biocide; admit that chlorine dioxide has utility in water treatment and disinfection and further admit that chlorine dioxide is typically generated on-site at the

point-of-use because of difficulties associated with its transportation. The DWW Parties deny the remaining allegations set forth in Paragraph 11 of the First Amended Complaint.

12. DWW lacks sufficient information to form a belief as to the truth or falsity of the allegations set forth in Paragraph 12 of the First Amended Complaint, and therefore denies them.

13. The DWW Parties admit Mr. DiMascio was an employee of Halox. The DWW parties lack sufficient information to form a belief as to the truth or falsity of the remaining allegations set forth in Paragraph 13 of the First Amended Complaint, and therefore denies them.

14. The DWW Parties lack sufficient information to form a belief as to the truth or falsity of the allegations set forth in Paragraph 14 of the First Amended Complaint, and therefore denies them.

15. The DWW Parties lack sufficient information to form a belief as to the truth or falsity of the allegations set forth in Paragraph 15 of the First Amended Complaint, and therefore denies them.

16. The DWW Parties admit that DWW has sold ClO₂ generator products to Nalco. The DWW Parties deny the remaining allegations of Paragraph 16 of the First Amended Complaint.

17. The DWW Parties admit they have filed suit in 2003 in the Western District of Texas against some of the IDEX Parties, and that such suit was transferred to the District of Connecticut and proceeded as an action captioned Halox Technologies, Inc., et al. v. Dripping Wet Water, et al., Civil Action No. 3:03-CV-1008 (“the 2003 litigation”) and that

Exhibit “A” is a true and correct copy of a Counterclaim filed by the DWW Parties in such action. The DWW Parties deny the remaining allegations set forth in Paragraph 17 of the First Amended Complaint.

18. The DWW Parties admit that the 2003 litigation was settled pursuant to the terms and conditions set forth in a Settlement Agreement dated May 26, 2006 (“the Settlement Agreement”). Further, the DWW Parties admit that a true and correct copy of said Settlement Agreement is appended to the First Amended Complaint as Exhibit “B”. The DWW Parties deny the remaining allegations as set forth in Paragraph 18 of the First Amended Complaint.

19. The DWW Parties admit that a lawsuit was filed on June 22, 2007 in the Western District of Texas captioned Dripping Wet Water, Inc., et al. v. IDEX Corporation, et al., Civil Action No. 5:-07-cv-531-XR and that a true and correct copy of the Complaint is appended as Exhibit “C” to the First Amended Complaint. The DWW Parties deny the remaining allegations as set forth in Paragraph 19 of the First Amended Complaint.

20. The DWW Parties deny the allegations set forth in Paragraph 20 of the First Amended Complaint except as to the identity of the parties shown in Exhibits “A” and “C” to the First Amended Complaint.

21. The DWW Parties admit the U.S. District Court for the District of Connecticut had jurisdiction over the parties named in Exhibit “A” to the First Amended Complaint. The DWW Parties deny the remaining allegations as set forth in Paragraph 21 of the First Amended Complaint.

22. The DWW Parties deny the allegations of Paragraph 22 of the First Amended

Complaint.

23. The DWW Parties deny the allegations of Paragraph 23 of the First Amended Complaint.

CLAIM FOR RELIEF

24. The DWW Parties incorporate by reference the allegations contained in Paragraphs 1 through 23 above, as if fully set forth hereat.

25. The DWW Parties deny the allegations of Paragraph 25 of the First Amended Complaint.

26. The DWW Parties deny the allegations of Paragraph 26 of the First Amended Complaint.

27. The DWW Parties deny the allegations of Paragraph 27 of the First Amended Complaint.

AFFIRMATIVE DEFENSES

In addition to the foregoing denials and admissions, the DWW Parties allege the following factual background and affirmative defenses:

FACTUAL BACKGROUND

28. No court has ever adjudicated the merits of DWW's inventorship and ownership claims as to the DiMascio Patents and applications ("the DiMascio Patets") here in issue. The Judgment entered in the 2003 litigation is but a two page document, incorporating the Settlement Agreement by reference, not mentioning any of the substantive issues raised by the DWW parties, nor the Idex parties.

29. The District Court in the 2003 litigation neither found inventorship , nor ownership, of the DiMascio Patents , nor did the District Court decide the merits of the DWW parties' claims set forth in Exhibit C and the Counterclaim alleged herein.

30. The Settlement Agreement does not objectively manifest an intent by the parties to cement their agreement with claim preclusion. The Settlement Agreement manifests an opposite intent.

31. The Settlement Agreement is not a complete settlement of all claims, reading, in relevant part:

Recitals, at paragraph 3 ; and as stated in the following terms :

3. Dismissal of Litigation. The Parties stipulate and agree that the Litigation, Halox Technologies, Inc.'s Second Amended Complaint, and the DWW Parties' Counterclaim, shall each be dismissed with prejudice. The Parties agree to execute a stipulation to dismiss, substantially in the form of Exhibit A hereto, and shall cooperate with each other in the filing of the stipulation and the dismissal of the Litigation with prejudice.

4. Declaration of Ownership. The Halox Parties acknowledge and agree that DWW is the owner of patent application 09/919,918.

5. Reservation of Rights. Except as stated in paragraph 4 above, each Party to this Agreement each fully reserves any and all rights such Party or its assignees and licenses may have as to claims and defenses related to patent interference proceedings and any alleged patent infringement.

In fact, the language of the Settlement Agreement expressly reserves "...any and all rights such Party or its assignees and licenses may have as to claims and defenses related to patent interference proceedings and any alleged patent infringement."

32. In short, the language of the Settlement Agreement is, not conclusive as to any issues as to inventorship and ownership of the DiMascio Patents. There is simply no

support for finding that a judgment pursuant to the Settlement Agreement gave it any preclusive teeth.

FIRST AFFIRMATIVE DEFENSE
(Failure to State a Cause of Action)

1. As a first and separate affirmative defense to the cause of action asserted in the Amended Complaint, the Amended Complaint fails to state facts sufficient to constitute a cause of action against the DWW Parties.

SECOND AFFIRMATIVE DEFENSE

2. As a second and separate affirmative defense to the cause of action asserted in the Amended Complaint, the Amended Complaint fails to state a claim upon which relief can be granted against the DWW Parties, because the DWW Parties have not performed any act that constitutes a violation of the parties' Settlement Agreement.

THIRD AFFIRMATIVE DEFENSE

(Bad Faith Law Suit)

3. As third and separate affirmative defense to the cause of action asserted in the Amended Complaint, the Amended Complaint is barred in that the IDEX Parties have commenced and continued this lawsuit without any facts or other reasonable basis supporting the purported claim set forth therein, and solely for the purpose of harassing and/or inducing improper payment and/or demand for relief from the DWW Parties.

FOURTH AFFIRMATIVE DEFENSE

(Good Faith and in Fair Competition)

4. As a fourth and separate affirmative defense to the cause of action asserted in the Amended Complaint, at all times relevant hereto, each and every act of statement made by the DWW Parties, with reference to some or all of the purported acts set forth in the Amended Complaint herein were made reasonably and in good faith and in fair competition.

FIFTH AFFIRMATIVE DEFENSE

(Waiver)

5. As a fifth and separate affirmative defense to the cause of action asserted in the Amended Complaint, the IDEX Parties knowingly and voluntarily relinquished and waived any and all rights that such parties may have had arising from the allegations set forth in the Amended Complaint.

SIXTH AFFIRMATIVE DEFENSE

(Estoppel)

6. As a sixth and separate affirmative defense to the cause of action asserted in the Amended Complaint, the IDEX Parties' conduct estops such parties from asserting the purported claim alleged in the Amended Complaint.

SEVENTH AFFIRMATIVE DEFENSE

(Plaintiff's or Third Party's Fault)

7. As a seventh and separate affirmative defense to the cause of action asserted in the Amended Complaint, if the IDEX Parties suffered or sustained any

loss and/or damage, as alleged in the Amended Complaint, such loss or damage was the direct and proximate result of the acts and omissions of the IDEX Parties and/or other persons for whom the DWW Parties are not responsible.

EIGHTH AFFIRMATIVE DEFENSE

(Set-Off)

8. As a eighth and separate affirmative defense to the cause of action asserted in the Amended Complaint, in the event that the DWW Parties are found to be liable to the IDEX Parties for any of the things alleged in the Amended Complaint, the IDEX Parties' recovery will be barred or decreased due to the right of set-off by the amount to which the IDEX parties , and each of them, owes the DWW Parties .

NINTH AFFIRMATIVE DEFENSE

(Mitigation)

9. As a ninth and separate affirmative defense to the cause of action asserted in the Amended Complaint, the IDEX Parties' cause of action is barred to the extent that the IDEX parties have failed to mitigate, minimize or avoid any loss they allegedly sustained and any recovery must be reduced by that amount.

TENTH AFFIRMATIVE DEFENSE

(Amendment)

10. As a tenth and separate affirmative defense to the cause of action asserted in the Amended Complaint, the DWW Parties allege that they presently have insufficient knowledge or information to form a belief as to whether they may have additional, as yet unstated, defenses available. Therefore, the DWW Parties reserve herein the right to assert

additional defenses in the event the discovery indicates that such defenses would be appropriate.

ELEVENTH AFFIRMATIVE DEFENSE

(Uncertainty)

11. As an eleventh and separate affirmative defense to the cause of action asserted in the Amended Complaint, the Amended Complaint is uncertain.

TWELFTH-FOURTH AFFIRMATIVE DEFENSE

(Collateral Estoppel)

12. As a twelfth and separate affirmative defense to each and every cause of action asserted in the Amended Complaint, the IDEX Parties' cause of action is barred by the doctrine of collateral estoppel .

PRAYER FOR RELIEF

The DWW parties ,and each of them denies, that the IDEX parties , or any of them is entitled to be awarded any of the relief sought in Paragraphs A-D of its prayer for relief against the DWW patrties. Plaintiffs' prayer for relief should, therefore, be denied in its entirety and with prejudice, and Plaintiffs should take nothing. The DWW parties should be awarded their reasonable costs and attorney fees.

COUNTERCLAIMS

Pursuant to Federal Rule of Civil Procedure 13, Counterclaimants, hereby assert the following counterclaims against the IDEX parties and avers as follows:

PARTIES

1. Counterclaimant, Dripping Wet Water Corporation (“DWW”) is a Texas corporation, with its principal place of business at 141 Industrial #300, Boerne, Texas 78006.

2. Counterclaimant, Allison H. Sampson, is an individual residing at 29520 Red Bud Hill, Fair Oaks Ranch, Texas 78015.

3. Counterclaimant, Richard L. Sampson, is an individual residing at 29520 Red Bud Hill, Fair Oaks Ranch, Texas 78015.

4. On information and belief, Counterdefendant IDEX Corporation (“IDEX”) is a Delaware corporation with its principal place of business in Northbrook, Illinois. IDEX is a holding company that owns numerous separately incorporated businesses, including Defendant Halox Technologies, Inc. that manufacture and sell chlorine dioxide generators, pump products, dispensing equipment, and other industrial products.

5. Upon information and belief, Counterdefendant Eastern Plastics is the surviving corporation of a merger with Halox Technologies, Inc. (“Halox”) and is a Connecticut corporation, with its principal place of business in Bridgeport, Connecticut.

6. Upon information and belief, Counterdefendant Pulsafeeder Inc. (“Pulsafeeder”) is a Delaware corporation, with its principal place of business in Northbrook, Illinois.

7. Upon information and belief, Counterdefendant Felice DiMascio (“DiMascio”) is

an individual residing at 1 Webster Lane, Rocky Hill, Connecticut 06067-2067. DiMascio was, employed by Halox.

NATURE OF THE SUIT
JURISDICTION AND VENUE

8. This Court has jurisdiction in this action pursuant to 28 U.S.C. § 1331, 28 U.S.C. § 1332, 28 U.S.C. § 1338, 28 U.S.C. § 2201, and 35 U.S.C. § 256.

9. Venue is proper in this district pursuant to 28 U.S.C. §§ 1391(b), (c) and (d).

10. Counterdefendants are subject to the personal jurisdiction of this Court and they have instituted this action.

11. The court also has supplemental jurisdiction over the state law claims for unjust enrichment, fraud and intentional concealment, under the principles of pendent jurisdiction.

INTERSTATE COMMERCE

12. Counterdefendants' activities, including activities related to its illegal activities, are in the flow of and substantially affect interstate commerce.

13. Counterdefendants manufacture, ship, and sell chlorine dioxide generators and related products, which are at issue, across state lines. Counterdefendants reap substantial revenues from sales of such products, which are at issue herein .

14. Counterdefendants' purported exclusive ownership of certain U.S. patent rights relating to chlorine dioxide technology, as set forth herein, is a sham. Counterdefendants have knowledge that their asserted claims of exclusivity are baseless. Counterdefendants'

assertion of such exclusive patent rights is, and was intended, by Counterdefendants to harm the consuming public and to hinder competitors, including Counterclaimant DWW, in the relevant markets. In truth, the Sampson Plaintiffs are the inventors of the unique chlorine dioxide generator technology, copied by DiMascio .

FACTS
OVERVIEW

15. Chlorine dioxide (ClO₂) is a highly effective, environmentally friendly biocide used in a variety of disinfection applications. Because of transportation restrictions (US Federal law prohibits the transportation of liquid ClO₂), chlorine dioxide is always generated on-site at the point-of-use.

16. This chlorine dioxide in-situ technology has become a significant factor in the water treatment marketplace. Chlorine dioxide kills organisms in water, and then breaks them down into harmless by-products that are environmentally safe. For this reason, the technology is of interest to the respective parties and to the consuming public.

Counterclaimant DWW is a direct competitor of Counterdefendants Halox, IDEX and Pulsafeeder in the market for manufacture, distribution and sale of such chlorine dioxide generators and related products.

17. Counterclaimants bring this action, in part, under United States patent laws against Counterdefendants for illegal conduct, specifically targeting Counterclaimants, and adversely affecting the markets for chlorine dioxide generators and related products. As a result of Counterdefendants' conduct, Counterclaimants have sustained injury for which Counterclaimants seeks money damages and other appropriate relief to compensate Counterclaimants for the harm Counterclaimants suffered and injunctive relief to end

Counterdefendants' illegal conduct.

18. This action also seeks, in part, to correct the inventorship of certain U.S. patents and applications ("the DiMascio Patents") identified in Exhibit "1" hereto.

19. The DiMascio Patents erroneously name Counterdefendant DiMascio as the only inventor when, in fact, each Counterclaimant Allison H. Sampson and Richard L. Sampson ("the Sampson Counterclaimants") also made substantial contributions to the claimed inventions. Pursuant to 35 U.S.C. Sect. 116, the Sampson Counterclaimants are each entitled to recognition as co-inventors of the subject matter claimed in the DiMascio Patents. Counterclaimants further seek a declaratory judgment under the United States patent laws that Counterclaimants have an ownership interest in the DiMascio Patents.

20. Counterclaimants also bring this action under 28 U.S.C. § 1332, to recover damages, costs of suit, and reasonable attorneys' fees, against Counterdefendants for injuries sustained by Counterclaimants as a result of Counterdefendants' fraud and intentional concealment, and unjust enrichment as alleged herein.

21. The exclusive patent rights asserted by Counterdefendants are not just. Counterdefendants' patent rights, if any, were copied from Counterclaimants' technology. Moreover, Counterdefendants have admitted that Counterclaimants are the true owners of the unique technology set forth in Counterclaimants' patent application for the inventions entitled Methods for Making Chlorous Acid and Chlorine Dioxide, US Serial No. 09/919, 918, ("the '918 application") filed August 2, 2001. (Exhibit "2")

22. Counterdefendants have falsely represented to the consuming public, in

published media and elsewhere, that Counterdefendants have exclusive rights to the subject matter claimed in the Dimascio patents and/or that Counterdefendant DiMascio is the sole inventor of the subject matter claimed in the DiMascio patents.

Counterdefendants have accordingly misled the consuming public as to the true inventorship, and asserted exclusivity in such subject matter. Counterdefendants' statements are unfounded, deceptive and not true.

23. As a result of Counterdefendants' illegal conduct, Counterclaimants have sustained injury for which Counterclaimants seek money damages, injunctive relief, and other appropriate relief to compensate Counterclaimants for the harm Counterclaimants have suffered.

24. Various persons, partnerships, sole proprietors, firms, corporations and individuals not named as Counterdefendants in this lawsuit, and individuals, the identities of which are presently unknown, may have participated as co-conspirators with Counterdefendants in the tortious conduct alleged in this complaint, and have performed acts and made statements in furtherance of the alleged conspiracy to harm Counterclaimants.

25. Counterclaimants are informed and believe, and thereon allege, that at all times mentioned herein, Counterdefendants and each of them, were the agents and/or employees of each other, and in doing the things hereinafter alleged, were acting within the course and scope of such agency and/or employment; and, further that each of the acts alleged herein was done with the full knowledge, consent, advice and permission of each of the other Counterdefendants.

26. Counterclaimants are informed and believe and thereon allege that, as set forth above and without limitation to other said further proof at the time of trial, Counterdefendants and each of them, knowingly and willfully conspired and agreed among themselves to damage Counterclaimants by, among other things and without limitation to proof, knowingly and willfully engaging in the tortious activities set forth herein .

27. Counterclaimants are informed and believe and thereon allege pursuant to such conspiracy, in furtherance thereof and without limitation to other and further proof, said Counterdefendants committed the acts stated herein.

28. Counterclaimants are informed and believe and based thereon allege that these acts were participated in, and performed by, one or more of said Counterdefendants as act in furtherance of such conspiracy, and for the unlawful and improper purposes stated herein.

29. Counterclaimants are informed and believe and based thereon allege, that in doing the tortious acts alleged herein, said Counterdefendants and each of them acted in a malicious and oppressive manner, with a conscious disregard for the rights of Counterclaimants, and that such conduct warrants an award of punitive damages against said Counterdefendants in an amount to be determined at the time of Trial.

PARTICULAR ALLEGATIONS

30. ClO_2 is a dissolved gas that is a strong biocide at concentrations as low as 0.1 ppm. ClO_2 can greatly reduce and eliminate biofilm populations and discourages bacterial re-growth. ClO_2 is a neutral species; it does not form weak acids as chlorine and bromine

do and, therefore, is effective over a wide pH range. ClO_2 is more efficacious than other oxidizing biocides and is compatible with most water treatment chemistry.

31. ClO_2 has consistently been shown to be the best molecule for controlling the causation organism of Legionnaires' disease. In the UK, the Building Services Research and Information Association (BSRIA) has recommended ClO_2 as the best available technology of control of Legionella in hot and cold water systems and the technology is taking hold in the United States.

32. ClO_2 is more efficacious than other biocidal technologies. It attacks pathogens on initial application and then leaves a residual of ClO_2 to discourage re-infection.

a) Potable Water: ClO_2 is EPA-approved for both pretreatment and final disinfection of drinking water. In pre-treatment, it effectively removes iron and manganese and promotes flocculation. It also removes noxious taste and odors as well as disinfectant byproduct precursors that can form trihalomethanes (THM's) and haloacetic acids (HAA's). In post-treatment, it provides a lasting residual throughout the distribution system. ClO_2 is ideal for hospital water systems, small water supplies, cisterns, and water purification membrane systems.

b) Cooling Towers: ClO_2 controls algae, planktonic bacteria, and biofilm promoting maximum efficiency for heat exchangers and ancillary equipment. It provides lasting residual throughout the distribution system. ClO_2 is more efficacious than other oxidizing biocides and compatible with most water treatment chemistry.

c) Water Treatment and Odor Control: ClO_2 safely oxidizes phenols, cyanides, aldehydes, and mercaptans, reduced sulfur compounds and some pesticides. It is useful in waste treatment and scrubber systems.

33. Counterclaimants are the owners of a unique technology for generating Chlorine Dioxide through Ion Exchange in contrast to conventional Electro-Chemical Technology. As set forth in disclosure of the Sampson Counterclaimants' '918 application, in contrast to conventional electro-chemical methods, Counterclaimants unique technology provides chlorous acid generated from a chlorite salt precursor. Ion exchange material facilitates the generation of chlorous acid by simultaneously removing unwanted cations from

solution and substituting hydrogen ion into the solution. Chlorine dioxide is generated in a controlled manner from chlorous acid by catalysis. Chlorine dioxide can be generated either subsequent to the generation of chlorous acid or simultaneously with the generation of chlorous acid.

34. In commercial use, Counterclaimants' CLO II Generator products, embodying this technology, take the hassle out of conventional electro-chemical chlorine dioxide generators. Counterclaimants' CLO II Generators use no chemical mixing chemistries and no electrochemical cassettes in their design. The CLO II Generators can dose directly into pressurized lines, and operators don't have to worry about storage of high concentration solutions or chlorinated byproducts. Counterclaimants' unique technology is particularly well suited for cooling tower applications.

35. On October 9 through 13, 2001 Counterclaimants first publicly exhibited their generator products at a trade show in Dallas, Texas sponsored by the Association of Water Technologies (AWT). To help explain this unique technology to the consuming public, Counterclaimants distributed marketing literature to the attendees describing the advantages of Counterclaimants' ion exchange technology in contrast to conventional electrochemical generation used by competitors.

36. On information and belief, Counterdefendants attended the 2001 AWT Expo and received Counterclaimants' literature which disclosed Plaintiffs' unique technology.

37. On March 22, 2002, Counterdefendant Idex entered into an Asset Purchase Agreement with third party sellers ("the third party Sellers") to acquire certain assets utilizing conventional electro-chemical chlorine dioxide technology.

38. For this transaction, Counterdefendant IDEX formed HT Acquisition Corporation, a wholly-owned subsidiary, to acquire the certain business assets (Electro-Chemical Technology Halox) under the Asset Purchase Agreement. After the transaction, HT Acquisition Corporation changed its name to Halox Technologies, Inc., (Counterdefendant named herein) In connection with its purchase of the Halox assets Counterdefendant IDEX prepared a comparison chart contrasting Halox electrochemical technology with Plaintiff's unique ion exchange technology.

39. Soon after the closing of the purchase contemplated by the Asset Purchase Agreement, Counterdefendant IDEX, learned of numerous draw backs associated with Halox electrochemical technology. Counterdefendants IDEX and Pulsafeeder quickly developed a severe case of "Buyer's Remorse".

40. By July 2003, Counterdefendant IDEX had claimed that it has suffered millions of dollars in losses arising from its acquisition of the conventional Halox technology. Counterdefendant IDEX alleged it suffered such economic losses including:

a) To repair the design and operating defects, IDEX and HTI have incurred hundreds of thousands of dollars in otherwise unnecessary travel expenses and consultants' fees, as well as substantial retrofit expenses. Further, IDEX and HTI have devoted substantial personnel time—more than 4,000 working hours—to remedy or otherwise compensate for the undisclosed flaws in the products embodying the electrochemical technology.

b) With respect to the non-existent regulatory approval, IDEX and HTI were forced to devote substantial resources, attempting to secure the approvals that the third party sellers represented it had or failed to inform IDEX were needed.

c) Because the third party sellers' electrochemical generator products, customers, markets, and regulatory approvals were not as represented, IDEX and HTI have incurred operating losses in the millions of dollars.

41. Counterdefendant IDEX further claimed, the third party sellers, omitted to state the following material facts:

- a) That there were material problems and disputes with Halox customers;
- b) That there had been a material change in the business and operations of the acquired assets due to the deteriorating relationship with customers and technical problems experienced with the electrochemical generator products;
- c) That there were defects in design, materials, and manufacture of the acquired electrochemical generator products;
- d) That the third party sellers were aware of circumstances that were likely to cause the warranty expenses or other unreimbursed repair, maintenance and replacement expenses of the business to increase in the future.
- e) That the third party sellers had not obtained certain regulatory approvals that were necessary for then anticipated applications.

42. In short, Counterdefendants were saddled with the electrochemical HALOX technology purchased just a year and some months earlier. Moreover, Counterdefendants recognized the significant advantages of Counterclaimants' unique technology, particularly, in commercial cooling tower applications..

43. On September 18 through 21, 2002, Counterclaimants again exhibited their unique ion exchange generator technology at the AWT trade show in Orlando, Florida . Counterdefendants Idex, Pulsafeeder and Halox, were also in attendance. Specifically, during the AWT trade show Counterdefendants' representative Paul Beldham requested Counterclaimant Richard Sampson to provide a more detailed disclosure of Counterclaimants' unique technology and to demonstrate DWW's generator products to Defendants. Mr. Beldham stated to Mr. Sampson that he would like to find a way for Counterdefendants and Counterclaimants to "work together" and that Idex had a potential acquisition interest in Counterclaimants' technology. Based upon Mr. Beldham's representations, the Sampson Counterclaimants provided Counterdefendants representatives , Marta Broge, Steve Ebersohl and Mr. Beldham with more detailed disclosure of Counterclaimants' technology and proprietary business information during

the course of several hours. Such disclosure included significant advantages of Counterclaimants' generator products to the consuming public in the relevant market. At no time did Counterdefendants, or their respective representative, reveal to Counterclaimants their covert agreement and plan to copy Counterclaimants' technology, and for Counterdefendants to claim exclusive patent rights through fraudulent inventorship .

44. Unbeknownst to Counterclaimants, within days of receiving Counterclaimants' AWT trade show disclosure, on September 30, 2002, Counterdefendants representative , DiMascio filed a patent application in the U.S. Patent and Trademark Office Serial No. 10/065,259 (the '259 DiMascio application) claiming exclusive rights and claiming sole inventorship in Counterclaimants' technology. The '259 DiMascio application copied significant portions of Counterclaimants' technology disclosed to Counterdefendants and was filed without informing Counterclaimants. Counterdefendants have subsequently filed, or caused to be filed, other U.S. and foreign patent applications which claim priority and or correspond to the '259 Dimascio application . These patents and applications are collectively referred to as" the DiMascio Patents" and are set forth in Exhibit "1" hereto.

45. Shortly after the Orlando AWT trade show, Paul Beldham , telephoned Counterclaimant Richard Sampson to express Counterdefendants' interest in utilizing Counterclaimants' technology for cooling tower applications. Specifically, Mr. Beldham stated that Counterdefendant IDEX believed DWW's products to be synergistic with Counterdefendants' Halox generator products rather than competitive. Mr. Beldham further indicated IDEX was interested in purchasing DWW's products for resale;

obtaining a license from Counterclaimants to permit Counterdefendants to manufacture Counterclaimants' ion exchange generator products; or for Counterdefendants to acquire Counterclaimants' technology. Mr. Beldham stated his belief that "it would be a good fit" with Counterdefendants' Halox product and would allow Counterdefendants to enter into new segments of the market. Mr. Beldham stated "the cooling tower "market as one commercial application that Counterdefendants would like to exploit with Plaintiffs' technology. At no time during the course of Mr. Beldham's telephone discussion did he reveal to Counterclaimants Counterdefendants' covert agreement and plan to copy Counterclaimants' technology and for Counterdefendants to wrongfully claim such exclusive patent rights.

46. In late November 2002, Paul Beldham again telephoned Counterclaimant Richard Sampson to further express Counterdefendants interest in Counterclaimants' technology. During the course of Mr. Beldham's second telephone conversation with Richard Sampson, he requested permission to have Counterdefendant DiMascio visit Counterclaimants' facilities in San Antonio, Texas. The stated purpose for Counterdefendant DiMascio's visit to Counterclaimants' facilities was to further conduct due diligence before Counterdefendants could reach a license agreement, bundling agreement or outright acquisition of Counterclaimants' technology. At no time did Mr. Beldham reveal Counterdefendants' covert agreement and plan to Counterclaimants, nor did Mr. Beldham reveal that Counterdefendants filed, or caused to be filed, the '259 Dimascio application.

47. On December 18 and 19, 2002 pursuant to Counterdefendants' covert

agreement and plan, DiMascio met with Counterclaimants in San Antonio, Texas to obtain further disclosure and proprietary information from the Sampson Counterclaimants relating to Counterclaimants' unique generator product line and technology. Counterdefendant DiMascio stated to the Sampson Counterclaimants that his visit and requested disclosure was for Counterdefendants' due diligence in forming a cooperative business arrangement with Counterclaimants to commercially exploit Counterclaimants' unique technology. Based upon Counterdefendants' continuing representations, and that of DiMascio, the Sampson Counterclaimants provided Counterdefendants with further detailed disclosure of their unique technology, system costs, system components, system characteristics, pricing structure and marketing strategy. At no time did Dimascio reveal Counterdefendants' covert agreement and plan, nor the filing of the '259 Dimascio application.

48. At all times during the course of the foregoing discussions between Counterclaimants and Counterdefendants referred to in paragraphs 43 through 47 above, Counterdefendants represented to Counterclaimants that Counterdefendants were interested in forming a cooperative arrangement with Counterclaimants for Counterclaimants' technology. However, at no time during these discussions did Counterdefendants reveal to Counterclaimants that Counterdefendants had copied, and were planning to copy, Counterclaimants' technology for Counterdefendants to claim exclusive patent rights by fraudulently filing patent applications in the name of Counterdefendant DiMascio identified in Exhibit 1 hereto.

49. In truth, Counterdefendants filed, or caused to be filed, the' 259 Di Mascio

application on Septemebr 30, 2002. without notifying Counterclaimants.

Counterdefendants then utilized Plaintiffs' technology claimed in the DiMascio patents and/or licensed Counterclaimants' technology to third parties without notifying Counterclaimants. Accordingly Counterdefendants did not reveal, nor share the resulting sales revenue and/or licensing income with Counterclaimants.

50. Counterdefendants made these misrepresentations and omissions, set forth in paragraphs 43 through 49 above, in order to induce Counterclaimants to make detailed disclosures to Counterdefendants related to Counterclaimants' unique technology and applications in product market.

51. Counterclaimants reasonably relied on Counterdefendants' actions and information to their detriment in making such disclosures to Counterdefendants. Counterdefendants each knew that such representations and omissions did not accurately represent the facts concerning Counterdefendants intentions with respect to defrauding Counterclaimants of their technology and its commercial value. Accordingly, those misrepresentations and omissions constitute fraudulent misrepresentation and intentional concealment, and Counterclaimants are each entitled to damages as set forth herein.

52. On April 3, 2003, the '918 Sampson application was published as U.S. Patent Application Publication 2003/0064018A1.

53. In connection with the filing and prosecution of the Dimascio patents, Counterdefendants have presented, or caused to presented, materially false statements to the US Patent and Trademark Office as to DiMascio's sole inventorship of claimed subject matter and Counterdefendants' asserted exclusive ownership and patent rights.

Counterdefendants' misrepresentations are contained in Dimascio declarations dated January 25, 2005, July 12, 2006 and February 6, 2007 among other documents filed in the US Patent and Trademark Office.

COUNT I

**Addition of Inventors Pursuant to 35 U.S.C. § 256
(The DWW Parties - Against All Counterdefendants)**

1. The DWW parties incorporate the allegations in paragraphs 1 through 53 of the Counterclaim allegations as if fully set forth hereat.

2. CounterDefendant DiMascio is not the true and only inventor of the DiMascio Patents. The Sampsons Counterclaimants each also contributed in a substantial way to the conception of at least one claim of each of the DiMascio Patents. The failure to include the Sampson Counterclaimants as additional inventors was without deception on the part of Counterclaimants .

3. The Sampson Counterclaimants were unaware that Counterdefendant DiMascio had obtained patent protection on their invention until after the '259 DiMascio application issued as a patent on July 5, 2005. Further, Counterclaimants were not aware that subsequent patent applications filings of DiMascio patents had been made by Counterdefendants until the respective publication dates of such DiMascio patents as set forth in Exhibit 1. Counterdefendant DiMascio did not inform the U.S. Patent and Trademark Office ("USPTO") of the substantial contributions to the claimed invention made by the Sampson Counterclaimants .

4. Counterclaimants Allison Sampson and Richard Sampson should be added as

named inventors of the DiMascio Patents; Counterclaimant Dripping Wet Water ("DWW") should be added as an assignee on the DiMascio Patents; Counterclaimants Allison Sampson and Richard Sampson should be added as named inventors on any pending reissue, continuation-in-part, reexamination, or divisional application claiming priority from the DiMascio Patents or any other application from which the DiMascio Patents claim priority or any patent application currently filed or that will be filed claiming exclusive right to the technology disclosed and claimed in Counterclaimants' patent application 09/919,918; and require that Counterdefendants take all action required to name Counterclaimants Allison Sampson and Richard Sampson as applicants on any foreign counterpart patents to the DiMascio Patents or on any pending or future foreign counterpart applications thereto; and to recover damages for Counterdefendants' failure to name the Sampson Counterclaimants as joint inventors on the DiMascio Patents as they are rightfully entitled under the patent laws.

COUNT 2

Declaratory Judgment of Ownership Interest in the DiMascio Patents and/or Right to use Patents – (Against All Counterdefendants)

5. The Counterclaimants incorporate the allegations in paragraphs 1 through 53 of the Counterclaim and paragraphs 2 through 4 of Count 1, as if fully set forth herein.

6. Counterclaimants seek a declaratory judgment that Counterclaimants have an ownership interest in and to the DiMascio Patents and/or right to use such patents.

7. This cause of action arises under the patent laws of the United States, 35 U.S.C. § 1 et seq.

8. There is a substantial and continuing justifiable controversy between Counterdefendants on the one hand, and Counterclaimants on the other, as to Counterclaimants' ownership interest in and to the DiMascio Patents and/or right to use the DiMascio Patents.

9. Counterdefendants deny that Counterclaimants have any ownership interest in and/or right to use the DiMascio Patents.

10. The Sampson Counterclaimants have made significant contributions to the aforementioned technology. On information and belief, Counterdefendants received and utilized these contributions made by Counterclaimants.

11. The IDEX parties are also parties to a Settlement Agreement that provides, in pertinent part, as follows:

"This Settlement Agreement (the "Agreement") is entered into as of the 26th day of May, 2006, by and between Halox Technologies, Inc. IDEX Corporation, and Pulsafeeder, Inc. (collectively, the "Halox Parties"), on the one side, and Dripping Wet Water, Inc., Richard L. Sampson, and Allison H. Sampson (collectively, the "DWW Parties"), on the other side. The Halox Parties and DWW Parties are collectively referred to as the Parties to this Agreement.

RECITALS

1. The Halox Parties and DWW Parties are parties to an action entitled *Halox Technologies, Inc. v. Dripping Wet Water, Inc., Richard L. Sampson, and Allison H. Sampson*, presently pending in the United States District Court for the District of Connecticut as Case No. 3:03CV1009 (the "Litigation").

*

*

*

4. Declaration of Ownership. The Halox Parties acknowledge and agree that DWW is the owner of patent application 09/919,918..."

12. The above-mentioned action was dismissed with prejudice by Order filed June 6, 2006.

13. The totality of the circumstances surrounding Counterclaimants' technology claimed in the DiMascio patents, and the activities respecting that technology, demand that each Sampson Counterclaimant, and each of them, be declared as an owner of the DiMascio Patents and that each Counterclaimant be allowed to use that technology.

14. Counterdefendants' claim of ownership of Counterclaimants' technology as set forth in the DiMascio Patents is vigorously disputed by Counterclaimants.

15. Absent a declaration of rights by this Court, the assertions made by Counterdefendants will subject Counterclaimants to continuing uncertainty and damages to its business. To resolve the legal and factual questions raised by Counterclaimants and to afford relief from uncertainty and controversy which the assertions made by Counterdefendants have precipitated, Counterclaimants are entitled to declaratory judgment of its rights under 28 U.S.C. §§ 2201 and 2202.

COUNT 3

Unjust Enrichment – (The Counterclaimants - Against All Counterdefendants)

16. The Counterclaimants incorporate the allegations in paragraphs 1 through 53, 2 through 4 of Count 1, and 6 through 15 of Count 2, as if fully set forth herein.

17. Counterclaimants are each a co-owner of the DiMascio Patents founded upon their respective rights under the patent laws and the general principles of estoppel, equity and implied license.

18. Upon information and belief, Counterdefendants have provided third parties with a license to the DiMascio Patents and have otherwise illegally utilized

Counterclaimants' technology without consent and by selling products based on Counterclaimants' technology.

19. Counterdefendants' failure to include the Sampson Counterclaimants as inventors, and omitting Counterclaimant DWW as an assignee, has caused Counterclaimants to suffer damages.

20. Counterdefendants' failure to include the Sampson Counterclaimants as inventors, and omitting Counterclaimant DWW as an assignee, has caused Counterdefendants to be unjustly enriched.

21. As a direct and proximate result of Counterdefendants' tortious activities as described herein, Counterclaimants have sustained and will sustain the injuries herein described.

22. Counterdefendants' tortious activities were done knowingly, willfully and maliciously and with the intent to injure and oppress Counterclaimants, and therefore, Counterclaimants are entitled to recover exemplary and punitive damages.

23. Counterdefendants' claimed exclusive rights in Counterclaimants' technology is baseless.

24. The actions taken by Counterdefendants to copy and claim exclusivity to Counterclaimants' technology were specifically intended to harm Counterclaimants .

25. On information and belief, Counterdefendants have sought to illegally assert exclusive patent rights in the subject matter claimed in the DiMascio Patents .

COUNT 4

**Fraud and Intentional Concealment
(The Counterclaimants - Against All Counterdefendants)**

26. Counterclaimants incorporate by reference the allegations set forth in paragraphs 1 through 53, 2 through 4 of Count 1, 6 through 15 of Count 2, and 17 through 25 of Count 3, of this complaint with the same force and effect as if set forth herein in their entirety.

27. During the course of discussions set forth in paragraphs 43-47, Counterdefendants represented to Counterclaimants that Counterdefendants were interested in forming a cooperative arrangement with Counterclaimants for Counterclaimants' technology, which representations were false at the time they were made. Counterdefendants knew that such representations were false when Counterdefendants made them, and/or Counterdefendants made such representation recklessly and without regard for the truth. Counterdefendants intended that Counterclaimants would rely on such representations. Counterclaimants reasonably relied on Counterdefendants' representations to Counterclaimants' material detriment.

28. Counterdefendants intentionally failed to disclose material facts that were known only to Counterdefendants and that Counterclaimants could not have discovered. At no time during these discussions set forth in paragraphs 43-47, did Counterdefendants reveal to Counterclaimants that Counterdefendants had copied, and were planning to copy, Counterclaimants' technology for Counterdefendants to claim exclusive patent rights by fraudulently filing patent applications in the name of Counterdefendant DiMascio

identified in Exhibit 1 hereto. Counterclaimants did not know of the concealed facts. Counterdefendants intended to deceive Counterclaimants by concealing the facts as set forth herein. Counterclaimants reasonably relied on Counterdefendants' deception to their detriment.

29. As a direct and proximate result of Counterdefendants' tortious activities as described herein, Counterclaimantss have sustained and will sustain the injuries herein described.

30. Counterdefendants' tortious activities were done knowingly, willfully and maliciously and with the intent to injure and oppress Counterclaimants, and therefore, Counterclaimants are entitled to recover exemplary and punitive damages.

31. Counterdefendants' claimed exclusive rights in Counterclaimants' technology is baseless.

32. The actions taken by Counterdefendants to copy and claim exclusivity to Counterclaimants' technology were specifically intended to harm Counterclaimants.

33. On information and belief, Counterdefendants have sought to illegally assert exclusive patent rights in the subject matter claimed in the DiMascio Patents beyond any legitimate coverage of the issued claims .

34. Counterclaimants reliance on Counterdefendants' representations and concealments set forth in paragraphs 43 through 47 above, were a substantial factor in causing Counterclaimants' harm.

35. Counterclaimants have incurred attorney fees and other related expenses in having to respond to Counterdefendants' false and deceptive assertion of exclusive rights to

the subject matter claimed in the DiMascio patents and Counterdefendants have been unjustly enriched.

PRAYER

For the reasons alleged, the DWW Parties respectfully pray this Court grant the following relief:

1. A declaration pursuant to 35 U.S.C. § 256, that the Sampson Counterclaimants should be added as inventors on the DiMascio Patents. In addition, Counterclaimant DWW should be added as an assignee of the DiMascio Patents;
2. A declaration that the DWW Parties each have an ownership interest in and to the DiMascio Patents and/or has a right to use such patents;
3. A declaration this case as exceptional within the meaning of 35 U.S.C. § 285 and that this Court award the DWW Parties their attorney's fees and costs;
4. As to Counts 3, and 4, award the DWW Parties damages in an amount sufficient to compensate each Counterclaimant for harm suffered.
5. As to Count 4, the IDEX Parties' tortious activities were committed knowingly, willfully and maliciously and with the intent to injure and oppress the DWW Parties, and therefore, the DWW Parties are entitled to recover exemplary and punitive damages.
6. An award to the DWW Parties for their reasonable attorneys' fees and costs and prejudgment and post judgment interest, and
7. Award such further relief as the Court deemed just and necessary.

DEMAND FOR JURY TRIAL

The DWW Parties hereby request a trial by jury.

DATED: May 27, 2008

Respectfully submitted,

by


Frank Frisenda

**Leon I. Edelson
EDELSON IP LAW GROUP, LTD.
Bannockburn Executive Plaza
2275 Half Day Road, Suite 122
Bannockburn, Illinois 60015
Tele: 847/374-9797
Fax: 847/374-9799**

**Frank Frisenda (Admitted PHV)
FRISNDA, QUINTON & NICHOLSON
11601 Wilshire Blvd., Ste. 500
Los Angeles, CA 90025
Tele: 702/792-3910
Fax: 702/436-4176**

**Attorneys for Dripping Wet Water,
Allison Sampson and Richard Sampson**

EXHIBIT 1

EXHBIT "/"

<u>Appli. Filing Date</u>	<u>Serial No.</u>	<u>Title of Invention</u>	<u>Publication No.</u>	<u>Publication Date</u>	<u>Patent No.</u>	<u>Issue Date</u>
INVENTOR: FELICE DIMASCIO						
9/30/02	10/065,259	SYSTEM AND PROCESS FOR PRODUCING HALOGEN OXIDES	US2004/0071627A1	4/15/04	6,913,741 B2	7/ 5/05
7/17/02	10/514,175	ELECTROLYTIC PROCESS AND APPARATUS	US2005/0252786 A1	11/17/05		
8/12/03	10/604,712	ELECTROLYTIC PROCESS FOR GENERATING CHLORINE OXIDE	US2005/0034997 A1	2/17/05		
10/10/03	10/683,056	SYSTEMS AND METHODS FOR GENERATING CHLORINE DIOXIDE	US2005/0079121 A1	4/14/05		
2/ 5/04	10/773,797	SYSTEMS AND METHODS FOR GENERATING CHLORINE DIOXIDE	US2005/0079122 A1	4/14/05		
11/12/04	10/986,610	SYSTEM AND PROCESS FOR PRODUCING HALOGEN OXIDES	US2005/0095192 A1	5/ 5/05		
1/25/05	11/042,287	SYSTEM AND PROCESS FOR PRODUCING HALOGEN OXIDES	US2005/0163700 A1	7/28/05		
9/27/06	11/235,848	CATALYST ELEMENTS AND METHODS OF MAKING AND USING	US2006/0068986A1	3/30/06		
11/ 2/05	11/265,032	CATALYST COMPOSITE AND METHODS OF MAKING AND USING	US2006/0110311A1	5/25/06		

<u>Appli.</u> <u>Filing</u> <u>Date</u>	<u>Serial</u> <u>No.</u>	<u>Title</u> <u>of</u> <u>Invention</u>	<u>Publication</u> <u>No.</u>	<u>Publication</u> <u>Date</u>	<u>Patent</u> <u>No.</u>	<u>Issue</u> <u>Date</u>
5/ 1/06	11/414,936	CATALYST ELEMENT AND USE THEREOF	US2006/0292059A1	12/28/06		
6/12/06	11/451,208	PROCESSES FOR PRODUCING AN AQUEOUS SOLUTION CONTAINING CHLORINE DIOXIDE	US2006/0280673A1	12/14/06		
8/11/06	11/502,778	BIOFILM REDUCTION IN PRESSURE DRIVEN MEMBRANE- BASED WATER TREATMENT SYSTEM	US2007/0034570A1	2/15/07		

EXHIBIT 2



US007087208B2

(12) **United States Patent**
Sampson et al.

(10) **Patent No.:** **US 7,087,208 B2**
(45) **Date of Patent:** **Aug. 8, 2006**

(54) **METHODS FOR MAKING CHLOROUS ACID AND CHLORINE DIOXIDE**

(76) Inventors: **Allison H. Sampson**, 35 Grace View Dr., Easton, CT (US) 06612; **Richard L. Sampson**, 35 Grace View Dr., Easton, CT (US) 06612

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 259 days.

(21) Appl. No.: **09/919,918**

(22) Filed: **Aug. 2, 2001**

(65) **Prior Publication Data**

US 2003/0064018 A1 Apr. 3, 2003

(51) Int. Cl.
C01B 11/02 (2006.01)
C01B 11/08 (2006.01)

(52) U.S. CL. 423/472; 423/477; 423/478

(58) Field of Classification Search 423/472, 423/477, 478

See application file for complete search history.

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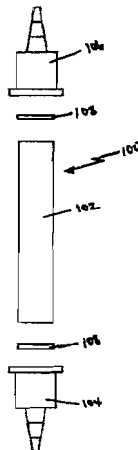
Primary Examiner—Ngoc-Yen Nguyen

(74) *Attorney, Agent, or Firm*—Jacobson Holman PLLC

(57) **ABSTRACT**

Chlorous acid is generated from a chlorite salt precursor, a chlorate salt precursor, or a combination of both by ion exchange. The ion exchange material facilitates the generation of chlorous acid by simultaneously removing unwanted cations from solution and adding hydrogen ion to solution. Chlorine dioxide is generated in a controlled manner from chlorous acid by catalysis. Chlorine dioxide can be generated either subsequent to the generation of chlorous acid or simultaneously with the generation of chlorous acid. For catalysis of chlorous acid to chlorine dioxide, the chlorous acid may be generated by ion exchange or in a conventional manner. Ion exchange materials are also used to purify the chlorous acid and chlorine dioxide solutions, without causing degradation of said solutions, to exchange undesirable ions in the chlorous acid and chlorine dioxide solutions with desirable ions, such as stabilizing ions, and to adjust the pH of chlorous acid and chlorine dioxide solutions.

29 Claims, 2 Drawing Sheets



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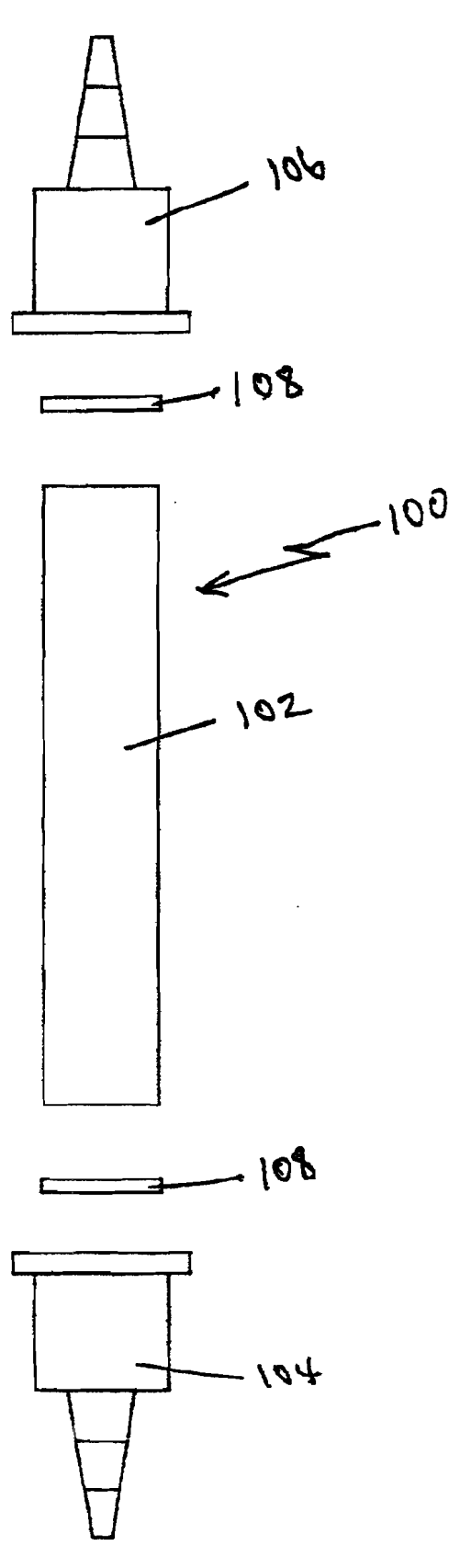
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FIG. 1



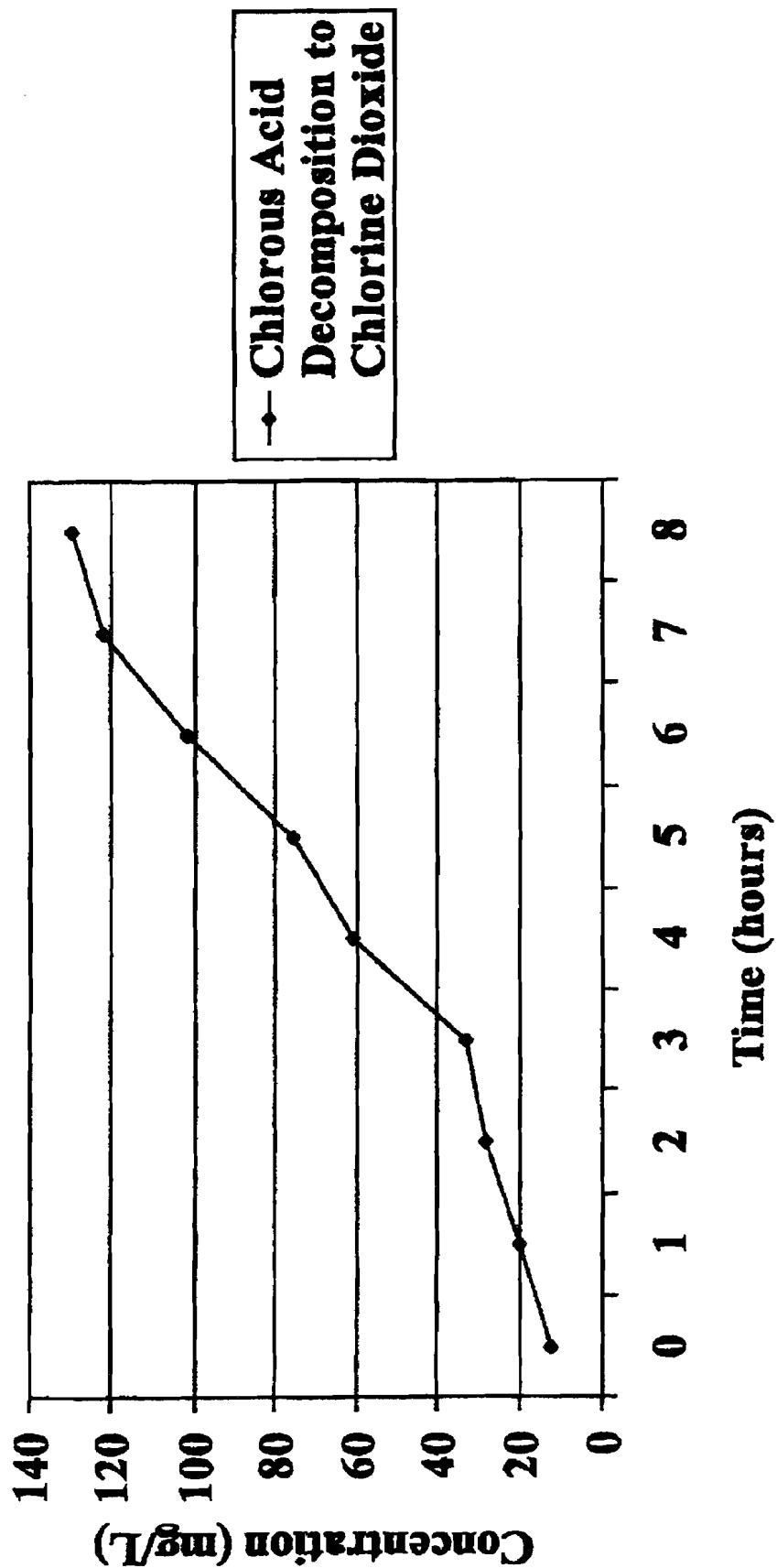
U.S. Patent

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Figure 2



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METHODS FOR MAKING CHLOROUS ACID
AND CHLORINE DIOXIDE

FIELD OF INVENTION

The present invention relates to a method for generating chlorous acid from an aqueous chlorite salt solution or an aqueous chlorate salt solution, or a combination of both solutions. The present invention also relates to a method for generating chlorine dioxide by means of catalysis of chlorous acid, either subsequent to or simultaneously with generation of the chlorous acid from a chlorite/chlorate salt solution.

BACKGROUND OF THE INVENTION

The generation of chlorous acid by the acidification of an aqueous chlorite salt solution or stabilized aqueous chlorine dioxide solution (stabilized chlorite salt solution) by an acid is well known by the following reaction:



It is also well known that over time, chlorous acid slowly decomposes to chlorine dioxide by the following reaction:



This reaction (2) predominates at low acid and high chlorite concentrations, making the reaction difficult to control, especially in high alkalinity water supplies. Further, this decomposition is slow. At chlorite concentrations greater than 20,000 mg/L, the reaction rate is 5 minutes at a pH<0.5. However, if the pH of the same chlorite solution is increased to >1.0, the reaction is not complete after 60 minutes.

It is also well known that in an oxidizing environment, such as in the presence of chlorine or an anode, chlorine dioxide can be generated from chlorous acid by the following reaction:



It is further known that chlorous acid is generated by the acidification of chlorate salt by the following two-step reaction:



In this reaction, hypochlorous acid, the ionized form of chlorine in water, is also generated reaction (5). The generation of chlorine dioxide occurs via the one of the following mechanisms:



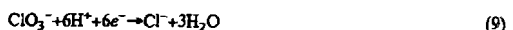
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or

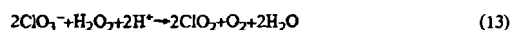
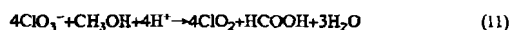


The generation of chlorine dioxide from chlorate salt, however, is very difficult to control. In practice, excess acidity is required to start the reaction, but if the acidity is too high, the following side reaction predominates, and little to no chlorine dioxide is generated.



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In practice, the following reduction reactions are used to generate chlorine dioxide from chlorate salt. High concentrations of all precursors must be used to start the reactions, but when the reactions do not go to completion, undesirable byproducts or unreacted precursor materials contaminate the chlorine dioxide solutions. In addition, the chloride ion must be present, either from the decomposition of chlorate or the addition of the chloride ion itself, for chlorine dioxide to be generated. Overall reactions for the generation of chlorine dioxide from chlorate are listed below.



It is further known that a mixture of chlorite salt and chlorate salt in the presence of hydrogen ion will generate chlorine dioxide by the following overall reaction:



This reaction is also shown in a different format in reaction (6). However, the rate of reaction to chlorine dioxide of the chlorite salt is 100 times faster than the rate of reaction to chlorine dioxide of the chlorate salt.

The use of chlorine dioxide in many applications has been limited due to the inability to control the reaction chemistries and the inefficiency of the reactions in solutions. Since chlorine dioxide is an unstable gas, even in solution, it must be generated on-site and used shortly after generation. Large-volume industrial applications such as pulp and paper bleaching, municipal water pretreatment and disinfection, food processing disinfection, and cooling tower disinfection have been successful due to the ability in these applications to safely handle concentrated and aggressive oxidizers and acids.

Some consumer and medical applications have also had success. Chlorite salt-based toothpastes, mouthwashes, and disinfecting skin gels use either the pH of the mouth or a weak-acid activator to slightly acidify the chlorite salt so that some chlorous acid is formed. The chlorous acid will then slowly decompose to chlorine dioxide by reaction (2).

It is also described in U.S. Pat. No. 6,200,557 B1 that in a topical solution designed to treat HIV, the chemical addition of phosphates will retard the loss of chlorine dioxide from solution at pH 6-7.4. This is especially beneficial in this topical application so that contact time of chlorine dioxide on the skin surface is increased to allow better treatment of the HIV.

However, in all of the prior art processes, controlling the reactions has remained a major obstacle. In addition, unreacted precursor components and reaction by-products are undesirably carried over into the product solutions. Also, in many instances, the pH of the product is so low due to the excess acid in solution that it cannot be used in certain applications.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been discovered that chlorous acid can be generated in a controlled manner from an aqueous chlorite salt solution or an aqueous chlorate salt solution, or a combination of both, by ion exchange. It has further been discovered that chlorine dioxide can be generated from chlorous acid by the use of at

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least one catalytic material. The chlorous acid for conversion to chlorine dioxide can be by ion exchange reaction in accordance with the present invention, or by conventional acidification. Preferred catalysts in accordance with the present invention include platinum, palladium, manganese dioxide, carbon and ion exchange material.

The chlorous acid may be generated separately in a first step and subsequently catalyzed to form the chlorine dioxide in a second step, or the chlorous acid and the chlorine dioxide may be generated simultaneously in the same reaction environment in the presence of the requisite catalyst. The process may be performed in either a continuous or a batch manner, and the reaction must be carried out in an aqueous solution or otherwise aqueous moist environment, i.e., in the presence of water or water vapor.

In the preferred embodiment of the present invention, the chlorous acid is generated by a salt cation/hydrogen ion exchange of chlorite salt or chlorate salt, or a combination of both, and the chlorous acid is then catalyzed in a moist environment to form chlorine dioxide either subsequently or simultaneously. Further, it has been found in accordance with the present invention, that chlorous acid, generated by the chemical acidification of chlorite salt or chlorate salt or both can also be catalyzed in a moist environment to form chlorine dioxide either subsequently or simultaneously.

In addition, it has been found in accordance with the present invention that additional precursors may be used with the chlorite salt solution or chlorate salt solution to enhance the catalysis of chlorous acid in a moist environment to form chlorine dioxide either subsequently or simultaneously. Such precursors include but are not limited to permanganate ion, chloride ion, sodium acid sulfite, peroxide and alcohol.

Still further, it has been found in accordance with the present invention that anion exchange materials are a preferred source of chlorite and/or chlorate ion, exchanged with a counter anion in a moist acidic environment to form chlorous acid, and further catalyzed in the moist environment to form chlorine dioxide either subsequently or simultaneously. By the ion exchange, a solution of chlorous acid can be generated from chlorite salt and/or chlorate salt by the salt cation/hydrogen ion exchange.

Additionally, ionic contaminants otherwise contained in the chlorous acid and/or chlorine dioxide solution can be removed with ion exchange, and ionic stabilizers may be added to the chlorous acid and/or the chlorine dioxide solutions via ion exchange. Still further, the pH of the chlorous acid and/or chlorine dioxide solutions may be adjusted by the use of ion exchange.

It is, therefore, an object of the present invention to generate chlorine dioxide from chlorous acid in the presence of at least one catalytic material in either a continuous or batch process in an aqueous solution or otherwise aqueous moist environment.

Another object of the present invention is to generate a chlorous acid solution generally free of cations, except hydrogen ion, in either a continuous or batch process, in an aqueous solution or otherwise aqueous moist environment.

A further object of the present invention is to generate chlorous acid and chlorine dioxide simultaneously in the presence of at least one catalytic material in either a continuous or batch process in an aqueous solution or otherwise aqueous moist environment.

A still further object of the present invention is to utilize an anion exchange material to supply chlorite ion and/or chlorate ion for the generation of chlorous acid in either a

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continuous or batch process in an aqueous solution or otherwise aqueous moist environment.

Still another object of the present invention is to purify the resulting chlorous acid and/or chlorine dioxide solution to remove any ionic contaminants by the use of ion exchange in either a continuous or batch process.

Yet a further object of the present invention is to adjust the pH of either the chlorous acid solution and/or the chlorine dioxide solution by use of ion exchange in either a continuous or batch process.

A final object of the present invention to be stated herein is to add ionic stabilizers to either the chlorous acid solution and/or the chlorine dioxide solution by using ion exchange in either a continuous or batch process.

These together with other objects and advantages, which will become subsequently apparent, reside in the details of the technology as more fully hereinafter described and claimed, reference being had to the accompanying drawings forming a part hereof, wherein like numerals refer to like parts throughout.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows an exploded elevational view of a plastic tube used in the tests of Examples 1-11 described in this application.

FIG. 2 is a graph showing the chlorine dioxide concentration versus time of a decomposing chlorous acid solution generated by ion exchange.

DETAILED DESCRIPTION OF THE INVENTION

In describing the present invention, specific terminology will be used for the sake of clarity. However, the invention is not intended to be limited to the specific terms so selected, or to the specific embodiments disclosed. It is to be understood that each specific term includes all technical equivalents, which operate in a similar manner to accomplish a similar purpose, and the specific embodiments are intended to illustrate, but not limit, the broad technical application and utility of the present invention.

As used herein, the term "solution" shall mean a mixture formed by a process by which a solid, liquid, or gaseous substance is mixed with a liquid, whether that liquid is a droplet, aerosol, vapor, or mist. Also, as used herein, the term "moist environment" shall mean that the environment in which the reaction occurs contains water moisture, ranging from a slightly humid environment to fully wet. Also, as used herein, the term "precursor" shall be used to mean any solution and/or combination of solutions used to generate chlorous acid and/or chlorine dioxide.

It is well known to those knowledgeable of the manufacture of chlorine dioxide that chlorous acid is formed by the acidification of chlorite salt and/or chlorate salt by the reactions (1), (4), and (5). In these reactions, hydrogen ion is placed in solution where it partially acidifies the chlorite salt and/or chlorate salt. The equilibrium conditions of the solution prevent the total acidification of the chlorite and/or chlorate salts, however, because sodium ion remains in solution. It has now been surprisingly found that if the sodium ion is replaced by a hydrogen ion by means of a cation exchange material, the equilibrium conditions of the solution change, and total acidification of the chlorite salt and/or chlorate salt is possible, thereby making a pure chlorous acid solution.

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Chlorous acid and aqueous solutions containing chlorous acid are particularly useful in applications where low-level disinfection over a long period of time is desirable. Some of these applications include disinfection of skin, the mouth, and cow teats. In addition, chlorous acid has a relatively low volatility level, making it applicable for surface disinfection in environments where off-gassing could be harmful. However, due to relatively high levels of residual chlorite in chlorous acid solutions and their inability to rapidly disinfect, chlorine dioxide is preferred in applications such as the disinfection of drinking water, cooling towers, food, and surfaces. In addition, chlorine dioxide is desirable for oxidizing organic contaminants and reducing iron and manganese levels in drinking water.

Further, it has been surprisingly discovered that a chlorous acid solution can be readily catalyzed to form chlorine dioxide. The source of the chlorous acid solution can be either that generated by ion exchange or by conventional acidification. If the latter, the catalytic conversion of the chlorous acid to chlorine dioxide drives the acidification reaction to completion or substantial completion.

By definition, catalysts work by changing the activation energy for a reaction, i.e. the minimum energy needed for the reaction to occur. This is accomplished by providing a new mechanism or reaction path through which the reaction can proceed. When the new reaction path has a lower activation energy, the reaction rate is increased, and the reaction is said to be catalyzed. When catalysis is used to generate chlorine dioxide from chlorous acid in the present invention, it was surprisingly found that neither high concentrations of precursor solutions nor high concentrations of chlorous acid were required to initiate the reactions. Further, it was surprisingly discovered that the reactions proceeded toward completion rapidly, thus decreasing the opportunity for undesirable byproducts or unreacted precursor materials to contaminate the chlorine dioxide solutions.

There are many catalysts that can be used within the scope of the present invention. These include, but are not limited to platinum, palladium, manganese dioxide, carbon, and ion exchange material. Further, it is well known that depositing such catalysts on various substrates, such as zeolites, aids in the catalysis by increasing surface area. Such catalysts are commercially available, and it is within the scope of those skilled in the art to choose an appropriate catalytic material and/or substrate to catalyze chlorous acid to chlorine dioxide.

Further, it has been discovered that an anion exchange material can be used to contribute a controlled amount of anions to the precursor, chlorous acid solution, and/or chlorine dioxide solution. For example, the chloride ion must be present for chlorous acid to be generated from a chlorate salt precursor. Although the necessary chloride may be present from the decomposition of chlorate, anion resin in the chloride form may be used to contribute additional chloride ion to the acidified chlorate salt precursor.

Ion exchange material can also be used to remove unwanted ions from the precursor, chlorous acid, and/or chlorine dioxide solution. For example, if the reaction to chlorine dioxide does not go to completion, unreacted chlorite and/or chlorate anion will be present in the chlorine dioxide solution. Anion exchange material can be used to remove the chlorite and/or chlorate ion. Further, if the precursor solution is acidified chemically, excess sodium ion will be present in the chlorine dioxide solution. Cation exchange material can be used to remove the sodium ion.

Ion exchange materials, such as inorganic and organic resins, membranes, powders, gels, and solutions are well

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known to those skilled in the art, and the type of ion exchange material used does not limit the invention. Examples of ion exchange materials are weak acid cation resins and powders, strong acid cation resins and powders, weak base anion resins and powders, strong base anion resins and powders, sulfonated polystyrene solutions, cation and anion selective membranes. Selection of a particular ion exchange material is considered within the skill of those knowledgeable in the field.

In one form of the present invention, cation exchange material is used to exchange the salt cation in a chlorite precursor with hydrogen ion to form chlorous acid. The resulting chlorous acid is then placed in contact with a catalytic material for a time sufficient to form chlorine dioxide. If the chosen catalyst is able to perform oxidation, such as manganese dioxide on the surface of greensand, reaction (3) predominates, and 100% of the chlorous acid can convert to chlorine dioxide. However, if the chosen catalyst is unable to perform oxidation, such as platinum, reaction (2) predominates, and only 80% of the chlorous acid can convert to chlorine dioxide.

In another form of the present invention, acid is added to the chlorite precursor to form chlorous acid with the salt cation still present in solution. The chlorous acid is then placed in contact with a catalytic material for a time sufficient to form chlorine dioxide. The choice of which acid to use depends upon the application. For example, if the chlorous acid and/or chlorine dioxide solution is to be used in a food processing application, an acid such as acetic acid may be preferred. If the chlorous acid and/or chlorine dioxide solution is to be used in a high purity industrial application, electrochemically-generated acid may be used. The choice of acid is well within the scope of knowledge of those skilled in this technology.

In another form of the present invention, an acidic reducing agent precursor is added to the chlorate precursor as the chlorate precursor is placed in contact with a catalytic material for a time sufficient to cause the generation of chlorous acid and chlorine dioxide simultaneously. If hydrochloric acid is used, it supplies both the acidity and the chloride required for the reaction. However, any acid source may be used, and the necessary chloride may come from the decomposition of the chlorate ion.

In another form of the present invention, an acid precursor and a reducing agent precursor are added to the chlorate precursor as the chlorate precursor is placed in contact with a catalytic material for a time sufficient to cause the generation of chlorous acid and chlorine dioxide simultaneously. Any acid source may be used, and the necessary chloride may come from the decomposition of the chlorate ion.

In another form of the present invention, a chlorate precursor is placed in contact with a cation exchange material mixed with a catalytic material. The salt cation in the chlorate precursor is exchanged with hydrogen ion as the chlorate precursor contacts both the cation exchange material and the catalytic material for a time sufficient to cause the generation of chlorous acid and chlorine dioxide simultaneously. If necessary, other precursors, such as sodium chloride, may be dosed along with the chlorate precursor to aid in the reaction.

In yet another form of the present invention, a reducing agent is placed in contact with the chlorate precursor either prior to the precursor being placed in contact with the catalytic material or as the precursor is placed in contact with the catalytic material for a time sufficient to form

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chlorine dioxide. In this form of the present invention, the catalytic material aids in reactions (10), (11), (12), and (13).

In another form of the present invention, a mixed chlorite and chlorate precursor is acidified as it is placed into contact with a catalytic material for time sufficient to form chlorine dioxide.

DESCRIPTION OF SPECIFIC EMBODIMENTS AND EXAMPLES

Precursor Solution for Examples 1-6

In Examples 1-6, a single chlorite precursor solution was used for all Examples. The chlorite precursor solution was prepared by diluting an aqueous 25% sodium chlorite solution with reverse osmosis water. The pH of the resultant solution was measured to be 8.5 with a Hach Sension 1 pH meter. The chlorite concentration in the precursor solution was measured to be 823 mg/L by using a Hach Digital Titrator, Iodometric Test Kit for Chlorine. To begin the measurement, 100 ml of reverse osmosis water was placed in a 250-ml Erlenmeyer flask, and 2 ml of the sample precursor solution was placed into the reverse osmosis water. One Potassium Iodide Powder Pillow and one Dissolved Oxygen Reagent 3 Pillow were added to the solution in the flask, swirled to mix, and placed in the dark for 10 minutes to allow the reaction to go to completion. Using a 0.113 N Sodium Thiosulfate Cartridge in the Digital Titrator, the solution was titrated to a pale yellow. Next, Starch Indicator Solution was added until the solution turned blue. The solution was titrated again until the solution remained colorless for 30 seconds. The titrator reading was recorded and divided by 800 to determine the milliliters of titrant used. Then the values were plugged into the following formula to determine the concentration of chlorite in the precursor solution:

$$\frac{\text{ml of titrant} \times \text{normality of sodium thiosulfate} \times 67,450}{\text{ml of sample} \times 4}$$

Plastic Testing Tubes for Examples 1-10

A sample of the plastic tubes used for carrying out the tests set forth in Examples 1-10 in the present application is shown in FIG. 1 and generally designated by reference numeral 100. The plastic test tube 100 includes a generally cylindrical body 102 having a conventional connection closure mounted at each end in the form of an inlet bottom connection 104 and an outlet upper end connection 106. Porex support media was cut to fit the inner diameter of the cylindrical tube 102, and a Porex disk 108 was placed at each end between the end of the cylindrical tubing 102 and the end closures 104 and 106 to act as support for the filling. The feed tubing ran to the inlet bottom connection 104 and outlet tubing ran from the outlet upper end connection 106.

Example 1

Chlorous Acid Generation by Cation Exchange

In Example 1, one 30 ml plastic test tube 100 as shown in FIG. 1 was clipped to a wall with pipe clips. The feed tubing

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ran from a reservoir containing the precursor solution to the bottom of the tube. The product tubing ran from the top of the tube to a brown sample bottle. In this example, the tube was filled with a commercially available strong acid organic cation resin in the hydrogen form, sold under the name Resintech CG-8, such that the tube was full.

A continuous stream of the chlorite precursor solution was passed upwardly through the tube such that the flow rate was 30 ml/min. A 250 ml sample of solution was taken from the tube's top end and placed in the brown bottle, sealed, and stored in a dark cabinet. A Hach 2010 Spectrophotometer using Method 8138 for the measurement of chlorine dioxide (0-700 mg/L) was used to test the stored sample for chlorine dioxide at one-hour intervals for eight hours.

The results of the foregoing test demonstrate, first, that chlorous acid may be generated from a chlorite precursor when placed in contact with a cation exchange material. Second, the development of chlorous acid to chlorine dioxide over time in this test are shown in FIG. 2, which demonstrates the slow reaction time for chlorous acid to decompose to chlorine dioxide.

Example 2

Chlorous Acid Generation by Cation Exchange from a Chlorite Precursor and Subsequent Catalytic Chlorine Dioxide Generation

In Example 2, two identical 30 ml plastic test tubes 100 as shown in FIG. 1 were clipped to a wall with pipe clips. Interconnecting plastic tubing ran from the first test tube to the second so that solution flowed from the bottom to the top of each test tube. The feed tubing ran from a reservoir containing the precursor solution to the bottom of the first test tube. The product tubing ran from the top of the second test tube to the flow-through cell of a Hach 2010 Spectrophotometer using Method 8138 for the measurement of chlorine dioxide (0-700 mg/L).

(A) The first test tube was filled with the Resintech CG-8 strong acid organic cation resin in the hydrogen form such that the tube was full. The second test tube was packed with a commercially available inorganic cation resin in the hydrogen form, sold under the name Resintech SIR-600, having platinum catalyst placed on the surface of the inorganic cation resin such that the tube was full. To place the platinum on the surface of the Resintech SIR-600 resin, a 100-ml solution of platinnic chloride was made such that the solution contained 1 gram of platinum. The platinnic chloride solution was then sprayed in a fine mist onto the surface of one liter of Resintech SIR-600 resin so as to form an even coating. The coated Resintech SIR-600 resin was then placed in an oven at 550° F. for three hours. Although platinnic chloride was used in this test, any soluble platinum salt could have been used for the coating material. Such salts and methods are well known to those schooled in the art of catalysis, and many are readily available as standard products. A continuous stream of the chlorite precursor solution was passed sequentially through the first and then the second test tube such that the flow rate was 30 ml/min.

(B) The first test tube was filled with the Resintech CG-8 strong acid organic cation resin in the hydrogen form such that the tube was full. The second test tube was packed with acid-washed carbon particles such that the drying tube was full. A continuous stream of the chlorite precursor solution was passed sequentially through the first and then the second test tube such that the flow rate was 30 ml/min.

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(C) The first test tube was filled with the Resintech CG-8 strong acid organic cation resin in the hydrogen form such that the tube was full. The second test tube was packed with acid-washed carbon particles having platinum catalyst placed on the surface of the acid-washed carbon such that the tube was full. The platinum was placed on the surface of the acid-washed carbon particles by the same method described in Example 2(A) above for depositing platinum on the surface of the cation resin. A continuous stream of the chlorite precursor solution was passed sequentially through the first and then the second test tube such that the flow rate was 30 ml/min.

(D) The first test tube was filled with the Resintech CG-8 strong acid organic cation resin in the hydrogen form such that the tube was full. The second test tube was packed with regenerated manganese greensand such that the tube was full. A continuous stream of the chlorite precursor solution was passed sequentially through the first and then the second test tube such that the flow rate was 30 ml/min.

(E) The first test tube was filled with the Resintech CG-8 strong acid organic cation resin in the hydrogen form such that the tube was full. The second test tube was packed with the Resintech SIR-600 inorganic cation exchange resin having manganese dioxide placed on the surface of the inorganic cation exchange material such that the tube was full. To place the manganese dioxide on the surface of the Resintech SIR-600 resin, a 100-ml solution of manganese sulfate was made such that the solution contained 1 gram of manganese. The manganese sulfate solution was then sprayed in a fine mist onto the surface of one liter of Resintech SIR-600 resin so as to form an even coating. The coated Resintech SIR-600 resin was then placed in an oven at 550° F. for three hours which converted the manganese to manganese dioxide. Although manganese sulfate was used in this test, any soluble manganese salt could have been used for the coating material. Such salts and methods are well known to those schooled in the art of catalysis, and many are readily available as standard products. A continuous stream of the chlorite precursor solution was passed sequentially through the first and then the second test tube such that the flow rate was 30 ml/min.

(F) The first test tube was filled with the Resintech CG-8 strong acid organic cation resin in the hydrogen form such that the tube was full. The second test tube was packed with a chlorite regenerated form of a commercially available organic anion exchange material having palladium on the resin, sold under the name Lewatit K7333 by Bayer Corporation, such that the tube was full. As purchased, the resin is in the hydroxyl form, but for this example, the resin was regenerated with sodium chlorite solution so as to place the resin in the chlorite form. A continuous stream of the chlorite precursor solution was passed sequentially through the first and then the second test tube such that the flow rate was 30 ml/min.

The results of the tests in Examples 2(A) through 2(F) are shown in the following Table 1.

TABLE 1

Example No.	Chlorine Dioxide Concentration (mg/L)
2 (A)	575
2 (B)	427
2 (C)	526
2 (D)	549
2 (E)	804
2 (F)	284

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Table 1 shows the concentration of chlorine dioxide after the chlorous acid from the first tube has been catalytically converted to chlorine dioxide in the second tube in the tests of Examples (A) through (F).

It will be seen that chlorous acid is significantly more readily converted to chlorine dioxide in the presence of a catalyst, as shown in all of Examples 2(A) through 2(F), compared to known chemical decomposition, as shown in Example 1, in which the chlorine dioxide concentration reaches only about 130 mg/L after eight hours, see FIG. 2.

Example 3

Simultaneous Generation of Chlorous Acid and Chlorine Dioxide by a Combination of Cation Exchange and Catalysis from a Chlorite Precursor

In Example 3, one 30 ml plastic test tube 100 as shown in FIG. 1 was clipped to a wall with pipe clips. The feed tubing ran from a reservoir containing the precursor solution to the bottom of the tube. The product tubing ran from the top of the tube to the flow-through cell of a Hach 2010 Spectrophotometer using Method 8138 for the measurement of chlorine dioxide (0-700 mg/L). In this example, the test tube 100 was packed with a 50/50 mixture of the Resintech CG-8 strong acid organic cation resin in the hydrogen form and the Resintech SIR-600 inorganic cation resin in the hydrogen form having platinum catalyst placed on the surface of the inorganic cation resin in the method as described above in Example 2(A) such that the test tube was full.

A continuous stream of the chlorite precursor solution was passed through the test tube such that the flow rate was 30 ml/min. The resultant concentration of chlorine dioxide from the test tube was 522 mg/L. It will thus be seen that the simultaneous generation of chlorous acid and chlorine dioxide readily occurs from a chlorite precursor solution in the presence of a cation exchange material and suitable catalyst.

Example 4

Simultaneous Generation of Chlorous Acid and Chlorine Dioxide by a Combination of Acidification and Catalysis from a Chlorite Precursor

In Example 4, one 30 ml plastic test tube 100 as shown in FIG. 1 was clipped to a wall with pipe clips. The feed tubing ran from a reservoir containing the precursor solution to the bottom of the test tube. The product tubing ran from the top of the test tube to the flow-through cell of a Hach 2010 Spectrophotometer using Method 8138 for the measurement of chlorine dioxide (0-700 mg/L). In this example, the test tube 100 was packed with the Resintech SIR-600 inorganic cation resin in the hydrogen form having platinum catalyst placed on the surface of the inorganic cation resin in the method as described above in Example 2(A) such that the test tube was full.

A continuous stream of the chlorite precursor solution was acidified to a pH of 2.5 and passed through the test tube such that the flow rate was 30 ml/min. The resultant concentration of chlorine dioxide from the test tube was 522 mg/L. It will thus be seen that the simultaneous generation of chlorous acid and chlorine dioxide readily occurs from an acidified chlorite precursor solution in the presence of a suitable catalyst.

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packed with the Resintech SIR-600 inorganic cation resin in the hydrogen form having platinum catalyst placed on the surface of the inorganic cation resin in the method described above in Example 2(A) such that the tube was full. A continuous stream of the chlorite precursor solution was passed sequentially through the test tubes such that the flow rate was 30 ml/min. The pH of the resultant solution was 2.4.

(B) In Example 7 (B), three 30 ml plastic test tubes 100 as shown in FIG. 1 were clipped to a wall with pipe clips. Interconnecting plastic tubing ran from the first test tube to the second and from the second to the third so that solution flowed from the bottom to the top of each tube. The feed tubing ran from a reservoir containing the precursor solution to the bottom of the first test tube. The product tubing ran from the top of the third test tube to the flow-through cell of a Hach 2010 Spectrophotometer using Method 8138 for the measurement of chlorine dioxide (0-700 mg/L). The first and second test tubes were filled as in Example 7(A). The third test tube was packed with an inorganic anion resin, hydrotalcite, in the phosphate form such that the tube was full. A continuous stream of the chlorite precursor solution was passed sequentially through the tubes such that the flow rate was 30 ml/min. The pH of the resultant solution was 7.8.

The results of the tests in Examples 7(A) and 7(B) are shown in the following Table 4.

TABLE 4

Example No.	Chlorine Dioxide Concentration (mg/L)
7 (A)	546
7 (B)	544

Table 4 shows the concentration of chlorine dioxide before and after the addition of a stabilizing ion. It will thus be seen that the concentration of chlorine dioxide is not affected when a stabilizing ion, such as phosphate, is added to the chlorine dioxide solution.

Example 8

Simultaneous Generation of Chlorous Acid and Chlorine Dioxide by a Combination of Cation Exchange and Catalysis from a Chlorate Precursor

In Example 8, a precursor solution was made containing both chlorate ion and chloride ion such that the concentration of the solution was 7,830 mg/L as chlorate and 4087 mg/L as chloride. The precursor solution was then placed in a reservoir and flowed through the apparatus.

One 30 ml plastic test tube 100 as shown in FIG. 1 was clipped to a wall with pipe clips. The feed tubing ran from a reservoir containing the precursor solution to the bottom of the test tube. The product tubing ran from the top of the tube to the flow-through cell of a Hach 2010 Spectrophotometer using Method 8138 for the measurement of chlorine dioxide (0-700 mg/L). In this example, the test tube was packed the same as in Example 3.

A continuous stream of the chlorate precursor solution was passed through the test tube such that the flow rate was 30 ml/min. The resultant concentration of chlorine dioxide from the test tube was 93 mg/L. It will thus be seen that a simultaneous generation of chlorous acid and chlorine dioxide from a chlorate precursor solution occurs in the presence of a cation exchange material and suitable catalyst.

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Example 9

Simultaneous Chlorous Acid and Chlorine Dioxide Generation using Ion Exchange and a Hydrochloric Acid Precursor

In Example 9, one 30 ml plastic test tube 100 as shown in FIG. 1 was clipped to a wall with pipe clips. The feed tubing ran from a gas-washing bottle containing 150 ml of a 30% hydrochloric acid precursor solution to the bottom of the test tube. The product tubing ran from the top of the test tube to a second gas-washing bottle that contained 200 ml of reverse osmosis water. The test tube was packed with a chlorate regenerated form of a commercially available organic anion exchange material having palladium on the resin, sold under the name Lewatit K7333 by Bayer Corporation, such that the tube was full. As purchased, the resin is in the hydroxyl form, but for this example, the resin was regenerated with sodium chlorate solution so as to place the resin in the chlorate form. The hydrochloric acid vapor was stripped from the hydrochloric acid precursor solution with compressed air and the vapor then flowed through the test tube. The final product from the test tube was sparged into the water in the second gas-washing bottle. The resultant solution from the second gas-washing bottle was tested for chlorine dioxide with a Hach 2010 Spectrophotometer using Method 8138 for the measurement of chlorine dioxide (0-700 mg/L).

A continuous stream of hydrochloric acid precursor vapor was passed through the test tube for 5 minutes. After 5 minutes, the concentration of chlorine dioxide was measured in the second gas-washing bottle. The resultant concentration of chlorine dioxide from the tube collected in the second gas-washing bottle was 187 mg/L. It will hence be seen that a simultaneous generation of chlorous acid and chlorine dioxide occurs in the presence of an acidic reducing agent, a suitable catalyst, and an anion exchange material in the chlorate form.

Example 10

Simultaneous Chlorous Acid and Chlorine Dioxide Generation using Ion Exchange and a Sodium Acid Sulfite Precursor

In Example 10, one 30 ml plastic test tube 100 as shown in FIG. 1 was clipped to a wall with pipe clips. The feed tubing ran from a gas-washing bottle containing 150 ml of a 20% sodium acid sulfite (NaHSO_3) precursor solution to the bottom of the test tube. The product tubing ran from the top of the test tube to a second gas-washing bottle that contained 200 ml of reverse osmosis water. The test tube was packed with the same organic anion exchange material in the chlorate form having palladium on the resin as described in Example 9 such that the tube was full. The sodium acid sulfite vapor was stripped from the sodium acid sulfite precursor solution with compressed air and the sodium acid sulfite vapor then flowed through the tube. The final product from the test tube was sparged into the water in the second gas-washing bottle. The resultant solution from the second gas-washing bottle was tested for chlorine dioxide with a Hach 2010 Spectrophotometer using Method 8138 for the measurement of chlorine dioxide (0-700 mg/L).

A continuous stream of sodium acid sulfite precursor vapor was passed through the tube for 5 minutes. After 5 minutes, the concentration of chlorine dioxide was measured in the second gas-washing bottle. The resultant concentra-

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tion of chlorine dioxide from the test tube collected in the second gas-washing bottle was 576 mg/L. It will therefore be seen that a simultaneous generation of chlorous acid and chlorine dioxide occurs in the presence of an acidic reducing agent, a suitable catalyst, and an anion exchange material in the chlorate form.

Example 11

Simultaneous Chlorous Acid and Chlorine Dioxide
Generation using an Ion Exchange Catalyst and a
Sodium Acid Sulfite Precursor

In Example 11, one 30 ml plastic test tube 100 as shown in FIG. 1 was clipped to a wall with pipe clips. The feed tubing ran from a gas-washing bottle containing 150 ml of a 20% sodium acid sulfite (NaHSO_3) precursor solution to the bottom of the test tube. The product tubing ran from the top of the test tube to a second gas-washing bottle that contained 200 ml of reverse osmosis water. The test tube was packed with a known inorganic anion resin, hydrotalcite, regenerated to be in the chlorate form, such that the drying tube was full. The sodium acid sulfite vapor was stripped from the sodium acid sulfite precursor solution with compressed air and the sodium acid sulfite vapor then flowed through the tube. The final product from the test tube was sparged into the water in the second gas-washing bottle. The resultant solution from the second gas-washing bottle was tested for chlorine dioxide with a Hach 2010 Spectrophotometer using Method 8138 for the measurement of chlorine dioxide (0-700 mg/L).

A continuous stream of sodium acid sulfite precursor vapor was passed through the test tube for 5 minutes. After 5 minutes, the concentration of chlorine dioxide was measured in the second gas-washing bottle. The resultant concentration of chlorine dioxide from the test tube collected in the second gas-washing bottle was 318 mg/L. It will thus be seen that a simultaneous generation of chlorous acid and chlorine dioxide occurs in the presence of an acidic reducing agent and a catalytic anion exchange material in the chlorate form.

The foregoing descriptions and examples should be considered as illustrative only of the principles of the invention. Since numerous applications of the present invention will readily occur to those skilled in the art, it is not desired to limit the invention to the specific examples disclosed or the exact construction and operation shown and described. Rather, all suitable modifications and equivalents may be resorted to, falling within the scope of the invention.

What is claimed is:

1. A process for generating chlorous acid which comprises contacting a chlorite salt solution with a cation exchange material in the hydrogen form in a moist environment for a time sufficient to effect an essentially complete substitution of cations in the chlorite salt with hydrogen ions on the cation exchange material to form chlorous acid.

2. The process as described in claim 1 wherein said cation exchange material is mixed with an additive.

3. A process for generating chlorous acid which comprises contacting a chlorate salt solution with a cation exchange material in the hydrogen form in a moist environment for a time sufficient to effect an essentially complete substitution of cations in the chlorate salt with hydrogen ions on the cation exchange material to form chlorous acid.

4. The process as described in claim 3 wherein said cation exchange material is mixed with an additive.

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5. A process for generating chlorous acid which comprises contacting a chlorate salt solution and an acid with an anion exchange material in a reducing ionic form in a moist environment for a time sufficient to form chlorous acid.

6. The process as described in claim 5 wherein said anion exchange material is mixed with an additive.

7. A process for generating chlorous acid which comprises contacting an acid with an anion exchange material in the chlorate form in a moist environment for a time sufficient to form chlorous acid.

8. The process as described in claim 7 wherein said anion exchange material is mixed with an additive.

9. A process for generating chlorous acid and chlorine dioxide which comprises contacting a chlorite salt solution with a cation exchange material in the hydrogen form and a catalytic material in a moist environment for a time sufficient to form chlorous acid and chlorine dioxide together.

10. The process as described in claim 9 wherein said catalytic material is on said cation exchange material.

11. The process as described in claim 9 wherein said catalytic material is an ion exchange material.

12. A process for generating chlorous acid and chlorine dioxide which comprises contacting a chlorate salt solution with a cation exchange material in the hydrogen form and a catalytic material in a moist environment for a time sufficient to form chlorous acid and chlorine dioxide together.

13. A process as described in claim 12 wherein said catalytic material is on said cation exchange material.

14. A process as described in claim 12 wherein said catalytic material is an ion exchange material.

15. A process for generating chlorous acid and chlorine dioxide which comprises contacting a chlorate salt solution and an acid with a catalytic material in a moist environment for a time sufficient to form chlorous acid and chlorine dioxide together.

16. The process as described in claim 15 wherein said catalytic material is on an ion exchange material.

17. The process as described in claim 15 wherein said catalytic material is an ion exchange material.

18. The process described in claim 15 wherein said catalytic material is an ion exchange material in a reducing ionic form.

19. A process for generating chlorous acid and chlorine dioxide which comprises contacting an acid with an anion exchange material in the chlorate form and one catalytic material in a moist environment for a time sufficient to form chlorous acid and chlorine dioxide together.

20. The process as described in claim 19 wherein said catalytic material is on said anion exchange material.

21. A process as described in claim 19 wherein said catalytic material is an ion exchange material.

22. The process as described in claim 19 wherein said acid is a reducing agent.

23. The process as described in claim 19 wherein said acid is mixed with a reducing agent.

24. The process as described in claim 9, wherein said moist environment is an aqueous solution of said chlorite salt solution.

25. The process as described in claim 9, wherein said catalytic material is selected from the group consisting of platinum, palladium, magnesium dioxide, carbon and ion exchange material.

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26. The process as described in claim 9, wherein said catalytic material is deposited on a suitable substrate to aid catalysis of said chlorous acid to said chlorine dioxide.

27. The process as described in claim 9, wherein said cation exchange material is a strong acid cation exchange material.

28. The process as described in claim 9, wherein said cation exchange material is selected from the group con-

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sisting of weak acid cation resins and powders, strong acid cation resins and powders, and cation selected membranes, or any combination of the foregoing.

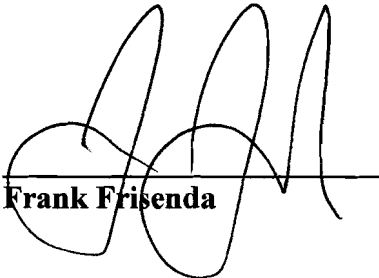
29. The process as described in claim 24, wherein said aqueous solution containing said chlorous acid and chlorine dioxide is used for disinfection.

* * * * *

CERTIFICATE OF SERVICE

I hereby certify that I have served a true and correct copy of THE DWW PARTIES' ANSWER, AFFIRMATIVE DEFENSES, AND COUNTERCLAIM upon the following attorney of record and the original upon the Clerk of the Court on this 27th day of May, 2008.

David K. Callahan
dcallahan@kirkland.com
Marcus E. Sernel
msernel@kirkland.com
KIRKLAND & ELLIS LLP
200 East Randolph Drive
Chicago, Illinois 60601-6636
Fax: 312/861-2200



Frank Frisenda